

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 1 219 731 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
03.07.2002 Bulletin 2002/27

(51) Int Cl. 7: C30B 29/16

(21) Application number: 00942454.9

(86) International application number:
PCT/JP00/04433

(22) Date of filing: 03.07.2000

(87) International publication number:
WO 01/16411 (08.03.2001 Gazette 2001/10)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

(72) Inventors:
• YOSHIDA, Hiroshi
Kawanishi-shi Hyogo 668-0111 (JP)
• SATO, Kazunori
Minoh-shi Osaka 562-0004 (JP)

(30) Priority: 01.09.1999 JP 24795999

(74) Representative: Wagner, Karl H., Dipl.-Ing.
Wagner & Geyer,
Patentanwälte,
Gewürzmunzstrasse 5
80538 München (DE)

(54) **FERROMAGNETIC p-TYPE SINGLE CRYSTAL ZINC OXIDE AND METHOD FOR
PREPARATION THEREOF**

(57) The present invention provides a single-crystal ZnO thin film having a high ferromagnetic transition temperature. In one aspect of the present invention, the ZnO thin film comprises a ferromagnetic p-type single-crystal zinc oxide including a transition metal element consisting of Mn, and a p-type dopant. In another aspect of the present invention, the thin film comprises a ferromagnetic p-type single-crystal zinc oxide including a transi-

tion metal element consisting of Mn, a p-type dopant, and an n-type dopant. The single-crystal zinc oxide material can be applied to quantum computers and high-capacity magnetic-optical recording medium by combining with conventional n-type or p-type transparent electrode ZnO materials or optical fibers, and to powerful information-communication devices or quantum computers as a photoelectric material usable for a wide range from visible light to ultraviolet light.

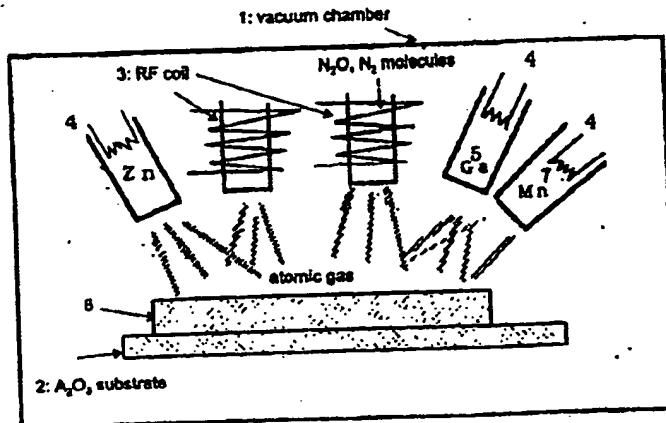


Fig. 1

Description

TECHNICAL FIELD

5 [0001] The present invention relates to a Mn-doped ferromagnetic p-type single-crystal zinc oxide material and a manufacturing method thereof.

BACKGROUND ART

10 [0002] Zinc oxide is a material having electrically semiconductive, photoconductive and piezoelectric properties. There has been known a method for producing through a sputtering or CVD process a zinc oxide material having suitable transparency and crystal-axis orientation for use as materials of piezoelectric or optoelectronics components (Japanese Patent Laid-Open Publication No. Hei 05-254991). A method has also been known for producing a transparent zinc oxide material having an electrically conductive or insulative property by doping zinc oxide of material with a doping material (Japanese Patent Laid-Open Publication No. Hei 05-070286). Further, a hydrothermal process has been known as a method for producing a piezoelectric semiconductor composed of a single crystal including zinc oxide as a primary component (Japanese Patent Laid-Open Publications No. Hei 06-279192, 06-279193, etc.). However, for such zinc oxide materials, it has not been reported to achieve a ferromagnetic state therein successfully.

15 [0003] Achieving a single-crystal ZnO thin film doped with Mn having a high ferromagnetic-transition temperature enables providing optical isolators or high-density magnetic recording medium capable of transmitting larger amount of information, and makes it possible to fabricate a desirable electronic industry material required for oncoming large-scale information transmission. ZnO also has a large band gap of 3.3 eV. This opens the way to fabricate a light-transmittable ferromagnetic material, which may facilitate the extensive evolution of manufacturing technologies for optical devices, such as a photon computer utilizing a coherent spin state.

20 [0004] For achieving a ferromagnetic state with a high ferromagnetic-transition temperature by doping Mn into ZnO, it is required to heavily dope a hole (p-type carrier) having an interactional function for ferromagnetically uniform the spin in Mn doped into ZnO being a wide-gap semiconductor.

DISCLOSURE OF INVENTION

30 [0005] In order to achieve the above object, the inventors have successfully developed a new method for controlling valence electron based on doping a p-type dopant by itself or codoping a p-type dopant and an n-type dopant, so as to ferromagnetically uniform the spin in Mn doped into ZnO, by utilizing an energy gain arising from itinerant kinetic-energy of the hole doped at a high concentration.

35 [0006] More specifically, according to one aspect of the present invention, there is provided a ferromagnetic p-type single-crystal zinc oxide (ZnO) material including Mn, which is a transition metal element acting as a leading part for generating ferromagnetism, and a p-type dopant (hole). In accordance with a principal that doping the p-type dopant into Mn-doped ZnO causes reduced kinetic energy along of the itinerant hole to provide a more stabilized ferromagnetic state than an antiferromagnetic or paramagnetic state, the p-type single-crystal zinc oxide material can be provided with a stable ferromagnetic critical temperature.

40 [0007] Further, according to another aspect of the present invention, there is provided a p-type ferromagnetic single-crystal ZnO material including Mn, which is a transition metal element acting as a leading part for generating ferromagnetism, and a p-type dopant (hole), wherein an n-type dopant is further included together with the p-type dopant. This facilitates achieving of the p-type single-crystal ZnO capable of providing significantly increased itinerant hole to enhance a ferromagnetic interaction between Mn ions.

45 [0008] The p-type dopant may be one or more components selected from a group consisting of C, N, and any suitable oxide thereof (e.g. CO₂, CO, N₂O, NO, or NO₃). The n-type dopant may be one or more components selected from a group consisting of B, Al, In, Ga, Zn, H, and any suitable oxide thereof (e.g. B₂O₃, Al₂O₃, In₂O₃, Ga₂O₃, or ZnO).

50 [0009] An entire ratio of Mn is incorporated into ZnO as a solid solution. Thus, the concentration of Mn included in the ferromagnetic p-type single-crystal ZnO material of the present invention can be set in the range of 1 to 99 mol%.

55 [0010] The ferromagnetic p-type single-crystal ZnO material of the present invention comprises a single crystal ZnO having a hole concentration of 1×10^{18} cm⁻³ or more, and a low resistance (1 Ω · cm or less). Increasing the hole concentration makes the doped-hole itinerant around Mn ions, and thereby the kinetic energy of the hole is reduced. This provides further stabilized ferromagnetic state and induces an enhanced ferromagnetic interaction between Mn ions.

[0011] The ferromagnetic p-type single-crystal ZnO material of the present invention has a ferromagnetic-transition critical temperature of 150 K or more. When Mn is doped into ZnO, Mn substitutes for sites of Zn having a radial size close to that of Mn with keeping a wurtzite structure, or Zn²⁺ is substituted by Mn²⁺. Thus, Mn goes into a high-spin

state having an electron spin S of 5/2. The ferromagnetic interaction between respective spins can be controlled by adjusting the Mn concentration.

[0012] The ferromagnetic transition temperature is increased in connection with the increase of the Mn concentration and hole concentration. This allows the ferromagnetic transition temperature to be changed flexibly from higher temperature to lower temperature according to need by adjusting the Mn concentration and the doped-hole concentration.

[0013] According to still another aspect of the present invention, there is provided a method for manufacturing the aforementioned ferromagnetic p-type single-crystal ZnO material, in which when an atomic gas from a solid-state source of Zn or Zn oxide and an activated oxygen are supplied onto a semiconductor substrate to grow a single-crystal zinc-oxide thin film on the substrate, in a thin film forming process such as the MOCVD process or MBE process, an atomic p-type dopant and an atomic Mn are supplied all together onto the substrate and deposited under a low temperature thereon.

[0014] The solid-state source of Zn or Zn oxide may include a pure zinc powder and a ZnO sintered material.

[0015] Preferably, the substrate has a temperature in the range of 300°C to 800°C. The temperature less than 300°C causes significantly lowered growth rate of the thin film, resulting in degraded practicability. The temperature higher than 800°C leads to intensive release of oxygen and increased defects. This causes degraded crystallizability and lowered doping effect. The substrate may include a silicon single-crystal substrate, a silicon single-crystal substrate formed with SiO, a sapphire single-crystal substrate. Preferably, the substrate has the same crystal structure as that of ZnO and substantially the same lattice constant as that of ZnO. There is no significant difference between the above substrates. Further, a chromium oxide layer or titanium oxide layer having an average value of respective lattice constants of the substrate and thin film may be interposed therebetween to reduce un conformity in crystal lattice.

[0016] In the method for manufacturing the aforementioned ferromagnetic p-type single-crystal ZnO material of the present invention, the concentration of the p-type dopant may be higher than that of the n-type dopant. This can be achieved, for example, by doping the n-type dopant with adjusting its implanted amount and the pressure of the atomic gas.

[0017] In the above manufacturing method, the ferromagnetic transition temperature of the zinc oxide material can be controlled by adjusting the Mn concentration and p-type dopant concentration (hole concentration) in the single-crystal zinc oxide material. The ferromagnetic critical temperature is increased as the Mn concentration and/or the doped-hole concentration are increased. Thus, the ferromagnetic transition temperature can be suitably controlled for any desired purpose according to the two adjustable parameters of the Mn and hole concentrations.

[0018] When the p-type dopant, n-type dopant or any oxide thereof, and/or Mn or any Mn oxide are doped, a radio beam, laser, X-ray or electron beam may be used to excite electronically to bring them into an atomic state.

[0019] ZnO is transparent because of its large band gap of 3.3 eV, and the life of its exciton is longer than that of GaN or the like. Thus, ZnO comes under the spotlight as a material of ultraviolet/blue lasers or ultraviolet/blue light emitting elements. However, in comparison with a low-resistance n-type ZnO material, it has been difficult to fabricate a p-type ZnO due to its unipolarity.

[0020] In the present invention, the n-type dopant such as Ga, Al, or In and the p-type dopant such as N are codoped, for example, by a ratio of 1:2. This allows ZnO to be doped at a high concentration to the extent of 10^{19} cm^{-3} to 10^{21} cm^{-3} , whereas in case of doping N by itself, ZnO is doped only to about 10^{18} cm^{-3} . With the resulting kinetic energy of the itinerant hole, the ferromagnetic state of Mn can be changed into a ground state to achieve further stabilized ferromagnetic state.

[0021] The electron spin S in Mn doped into ZnO is 5/2, and the exchange split (up to 3 eV) of Mn^{2+} (d5) is larger than the crystal field split (up to 0.8 eV) thereof, which shows that a desirable high-spin state is achieved. Doping a hole into such a system in a ferromagnetic state makes the doped-hole itinerant around Mn ions in a crystal without inverting any spin. Thus, the kinetic energy of the hole is reduced, and thereby the ferromagnetic state is more stabilized than an antiferromagnetic state.

[0022] In the antiferromagnetic state, it is required to invert the spin in order to make the doped-hole itinerant in the crystal. In addition to lots of energy for inverting the spin, a significant energy is required for the exchange interaction. Thus, generating the ferromagnetic state based on the doped-Mn with the itinerant doped-hole can provide an efficient electron-theoretical mechanism for stabilizing the ferromagnetic state more than the antiferromagnetic or paramagnetic state.

BRIEF DESCRIPTION OF DRAWINGS

[0023] Fig. 1 is a schematic side view showing an apparatus for manufacturing a Mn-doped ferromagnetic p-type single-crystal ZnO material through the MBE process.

[0024] Fig. 2 is a graph showing the density in electronic states of a ferromagnetic p-type ZnO material codoped with Mn as a transition metal element, Ga as a donor element, and N as an acceptor element.

BEST MODE FOR CARRYING OUT THE INVENTION

[0025] A method for forming a ferromagnetic p-type single-crystal ZnO thin film on a substrate through the MBE process will now be described based on an embodiment of the present invention.

Embodiment 1

[0026] As shown in Fig. 1, an Al_2O_3 substrate 2 was placed within a vacuum chamber 1 maintained in a constant vacuum of 10^{-6} Torr. Then, both atomic gases of Zn and O (oxygen) were supplied onto the substrate 2 to fabricate a ZnO thin film on the substrate 2. Zn and Mn to be used were prepared by heating each corresponding solid-state source having a purity of 99.99999 with a heater to bring them into an atomic state. For O and N to be used, the corresponding atomic gases having a purity of 99.99999 were prepared by activating O_2 and N_2O (or N_2) using an RF radical cell, respectively. N serving as the p-type acceptor was a nitrogen radical generated by a RF (13.56 MHz) excitation type radical beam source. Ga and Mn to be used were prepared by radiating the microwave level of electromagnetic waves to each corresponding molecular gas or by bringing each corresponding elemental cell into an atomic state under a high temperature. As components for used in this processing, Fig. 1 shows an RF (radio frequencies) coil 3, a heater 4, a elemental cell (Ga source) 5, and an elemental cell (Mn source) 7.

4, an elemental cell (Ga source) 5, and an elemental cell 6. [0027] During forming a film, while Ga as the n-type dopant, atomic N as the p-type dopant and atomic Mn were supplied all together along the surface of the substrate 2 at partial pressures of 10^{-7} Torr, 5×10^{-7} Torr and 10^{-7} Torr, respectively, desired crystal growth was induced at each temperature of 350°C, 400°C, 450°C, 600°C, and 750°C to form n-type single-crystal ZnO thin films 6.

[0028] Table 1 shows hole concentration measurements, Mn concentration measurements through the SIMS, and ferromagnetic transition temperature measurements through the SQUID and the measurement of magnetic coefficient, μ_m , for the Mn-doped ferromagnetic p-type single-crystal ZnO thin films obtained at the above respective crystal growth temperatures.

25 for each of the ferromagnetic p-type single-crystal ZnO thin film obtained at the above respective crystal growth temperatures.

Table 1

substrate temperature (°C)	acceptor concentration (cm⁻³) codoping of Ga and N	Mn concentration (mol%)	ferromagnetic transition temperature (K)
350	4x10¹⁸	5.2	150
400	6x10¹⁸	8.0	289
450	6x10¹⁸	12.4	389
600	8x10²⁰	25.3	520
750	8x10²¹	34.5	780

[0029] As can be seen from the dependence of the ferromagnetic transition temperature on the Mn concentration, the acceptor concentration, and the substrate temperature, higher concentrations of Mn and p-type carrier (hole) provides higher ferromagnetic transition temperature ($^{\circ}\text{K}$). Further, it can be seen that the ferromagnetic interaction between Mn ions tends to increase depending on the hole concentration, and the ferromagnetic interaction between Mn spins tends to increase in response to the increase of the Mn concentration.

[0030] Fig. 2 shows the density in electronic states of a ferromagnetic p-type single-crystal ZnO material doped with Mn at a high concentration. The exchange split between the majority spin and the minority spin is about 3 eV, and the crystal-field split is about 0.8 eV, which shows that a high-spin state ($S = 5/2$) has been achieved. The local magnetic moment at Mn sites is 4.8 Bohr magneton (μ_B) per Mn atom.

INDUSTRIAL APPLICABILITY

[0031] As described above, the present invention provides a novel ferromagnetic p-type single-crystal ZnO (zinc oxide) material including Mn and a p-type dopant (hole). This material can be applied to quantum computers and high-capacity magnetic-optical recording medium by combining with conventional n-type or p-type transparent electrode ZnO materials or optical fibers, and to powerful information-communication devices or quantum computers as an optoelectronic material usable for a wide range from visible light to ultraviolet light.

Claims

1. A ferromagnetic p-type single-crystal zinc oxide material including a transition metal element consisting of Mn, and a p-type dopant.
- 5 2. A ferromagnetic p-type single-crystal zinc oxide material including a transition metal element consisting of Mn, a p-type dopant, and an n-type dopant.
- 10 3. A method for manufacturing a ferromagnetic p-type single-crystal zinc oxide material as defined in claim 1, in which when an atomic gas from a solid-state source of Zn or Zn oxide and an activated oxygen are supplied onto a semiconductor substrate to grow a single-crystal zinc-oxide thin film on the substrate, an atomic p-type dopant and an atomic Mn are supplied all together onto the substrate.
- 15 4. A method as defined in claim 3 for manufacturing a ferromagnetic p-type single crystal zinc oxide material as defined in claim 2; in which the n-type dopant is doped so as to provide a higher concentration of the p-type dopant than that of the n-type dopant.

20

25

30

35

40

45

50

55

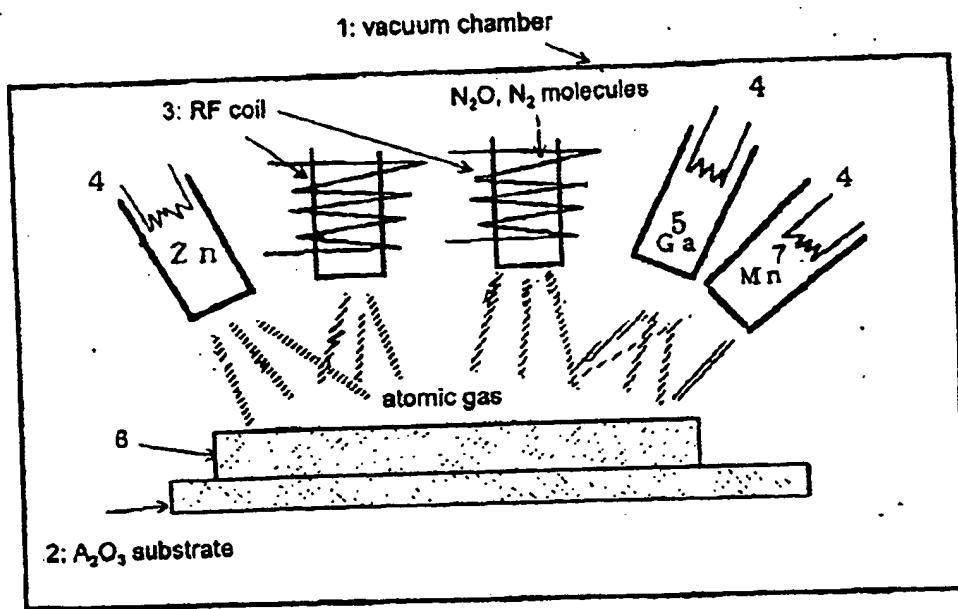


Fig. 1

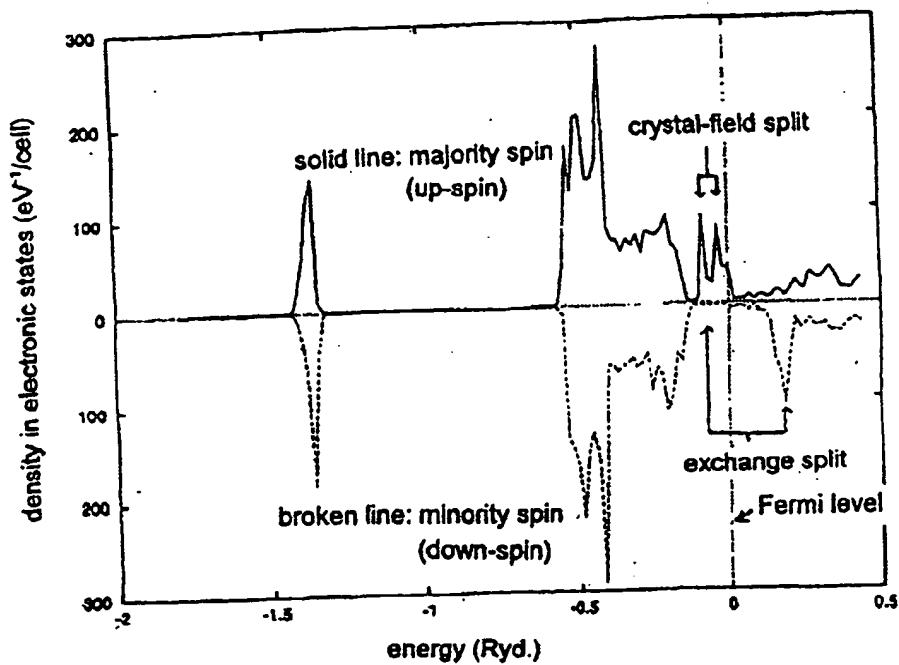


Fig. 2

INTERNATIONAL SEARCH REPORT		International application No. PCT/JP00/04433
A. CLASSIFICATION OF SUBJECT MATTER Int.Cl' C30B29/16		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl' C30B1/00-35/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Tokoku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Tokoku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE, "zinc or zinc(w) oxide, dope?, dopant?, resistance, p(w)type? or positive?" JICST FILE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	T. Yamamoto et al., "Solution Using a Codoping Method to Unipolarity for the Fabrication of p-Type ZnO", Japanese Journal of Applied Physics, Vol.38, part 2, No. 2B, 15.Feb.1999 (15.02.99), pp.166-169	1-4
A	K. Minegishi et al., "Growth of p-type Zinc Oxide Films by Chemical Vapor Deposition", Japanese Journal of Applied Physics, Vol. 36, part 2, No.11A, 1. November 1997 (01.11.97), pp.1453-1455	1-4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See parent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier document but published on or after the international filing date "C" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "D" document referring to an oral disclosure, use, exhibition or other means "E" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 03 August, 2000 (03.08.00)		Date of mailing of the international search report 15 August, 2000 (15.08.00)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

Mar 8, 2002

File: JPAB

Entry 1 of 15

IO: JP02002068890A
IDENT-IDENTIFIER: JP 2002068890 A
3: ZnO-BASED MATERIAL AND METHOD OF PRODUCING THE SAME

-DATE: March 8, 2002

INVENTOR-INFORMATION:

COUNTRY

3
ITA, KENICHI
ITA, SHIZUO
ITA, SHIGEO

LICENSEE-INFORMATION:

COUNTRY

E
SAI TLO KK

L-NO: JP2000265774

L-DATE: September 1, 2000

CL (IPC): C30 B 29/16; C23 C 16/40; H01 L 41/18; H01 L 41/24

ABSTRACT:

PROBLEM TO BE SOLVED: To produce a high quality epitaxial thin film of a single crystal zinc oxide free from stacking faults.

SOLUTION: A method of producing the epitaxial thin film of the single crystal zinc oxide comprises forming a first layer 3 being a buffer layer and comprising polycrystalline or amorphous ZnO at about 400 to 500°C on a sapphire substrate 2 by an organo-metal vapor phase growth method, then forming a second layer 4 comprising a single crystal ZnO at about 800°C on the first layer 3, partially forming a mask 5 of SiO₂ by a photo-lithography technique, further selectively growing the single crystal ZnO from each exposed part in the mask 5 of the second layer 4, and forming a third layer 6 of the single crystal ZnO grown in the horizontal direction on the mask 5 from the single crystal present above each exposed part 7. The terminating defects 11 in the second layer 4 are intercepted by the mask 5.

COPYRIGHT: (C) 2002, JPO

[Previous Doc](#)[Next Doc](#)[Go to Doc#](#)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:



BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.